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ABSTRACT

The treatment of wastewater phosphorus via land application includes both chemical and biological mechanisms. Chemically, phosphorus reacts with iron, aluminum, and calcium compounds in the soil providing efficient removal over a wide range of pH values. Phosphorus is also absorbed by rooted plants which, upon harvest, constitute a further removal mechanism. The general principles of phosphorus interactions between soil and wastewater are illustrated, and the mass balance is derived for a typical loading rate and application season. Soil P movement and retention are discussed, with particular reference to the chemical environment necessary to produce movement of phosphorus among the three possible categories: dissolved, labile, and fixed. Crop uptake and surface runoff are examples of other mechanisms of phosphorus removal which are discussed in this module. Application of domestic sewage effluents at a rate of 2 inches/wk for 30 weeks results in annual phosphorus additions of approximately 140 lb P/acre. At this rate, many soils are capable of efficient phosphorus removal for periods ranging from 20 to 50 years or more. Rapid infiltration systems, with annual applications of 1500 lb P/acre or more, are generally less efficient in phosphorus removal but vary considerably depending on specific site characteristics. Results from existing land application systems are cited to illustrate the basic principles of phosphorus removal. (Author/BB)

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Land Application

of Wastes

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PHOSPHORUS CONSIDERATIONS

Module 19

January, 1978

LAND APPLICATION
OF WASTES -
AN EDUCATIONAL PROGRAM

The objective of this program is to increase the knowledge of engineers, scientists, waste management specialists and other practitioners in the concepts and principles needed to properly utilize the potential of land for the application of wastes. It is designed for individuals concerned with waste disposal alternatives for municipal, industrial, and agricultural wastes. The modules in this Program incorporate knowledge from sanitary and environmental engineering, agronomy, soil science, agricultural engineering, economics, and law.

The program consists of some twenty-five modules and audio-visual materials as appropriate.

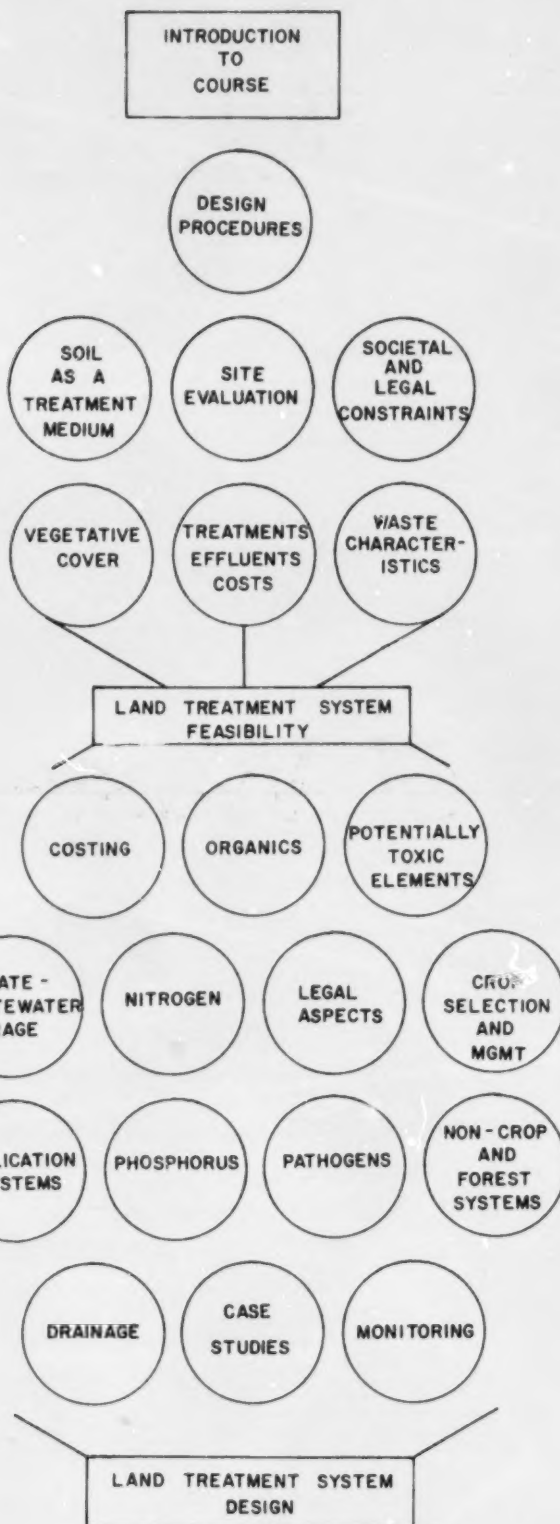
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PHOSPHORUS CONSIDERATIONS

Module 19

January, 1978

Summary

The treatment of wastewater phosphorus via land application includes both chemical and biological mechanisms. Chemically, phosphorus reacts with iron, aluminum, and calcium compounds in the soil providing efficient removal over a wide range of pH values. Phosphorus is also absorbed by rooted plants which, upon harvest, constitute a further removal mechanism.

The general principles of phosphorus interactions between soil and wastewater are illustrated, and the mass balance is derived for a typical loading rate and application season. Soil P movement and retention are discussed, with particular reference to the chemical environment necessary to produce movement of phosphorus among the three possible categories: dissolved, labile, and fixed. Crop uptake and surface runoff are examples of other mechanisms of phosphorus removal which are discussed in this module.

Adsorption isotherms provide a means of assessing short-term phosphorus retention capabilities in different soils. Such isotherms, however, do not account for relatively slow reversion reactions which render soil phosphorus compounds increasingly unavailable for leaching with time. Reversion reactions are favored by alternate application and resting periods.

Application of domestic sewage effluents at a rate of 2 inches/wk for 30 weeks results in annual phosphorus additions of approximately 140 lb P/acre. At this rate, many soils are capable of efficient phosphorus removal for periods ranging from 20 to 50 years or more. Rapid infiltration systems, with annual applications of 1500 lb P/acre or more, are generally less efficient in phosphorus removal but vary considerably depending on specific site characteristics.

Results from existing land application systems are cited to illustrate the basic principles of phosphorus removal.

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Objectives

After completing this module, the reader should be able to:

1. Describe common loading rates of phosphorus in land application systems and where the various forms of phosphorus found in wastewater come from.
2. Describe those soil conditions which favor the retention of phosphorus.
3. Discuss the availability of phosphorus in the soil and how phosphorus is retained in the soil in various forms.
4. Discuss how the land application site should be managed to enhance phosphorus removal.
5. Explain the usefulness and the limitations of adsorption isotherms in determining phosphorus retention of soil.
6. Discuss the relative effectiveness of spray irrigation, overland flow, and rapid infiltration systems for phosphorus removal.

Introduction

Phosphorus, like nitrogen, is an essential nutrient for the growth of plants and animals. Both nutrients are of major importance in determining levels of eutrophication in surface waters, with phosphorus often being the limiting nutrient. Increases in the phosphorus concentration of water entering lakes and streams will therefore tend to increase the probability and severity of "nuisance" plant growth.

Phosphorus and nitrogen, however, differ in their behavior within the soil. Under certain conditions, nitrogen is lost to the atmosphere through ammonia volatilization and denitrification, but there is no analogous gaseous loss of phosphorus. Even more important are differences in mobility of the two nutrients. Both exist in anionic forms (NO_3^- and H_2PO_4^- or HPO_4^{2-}) which are not subject to cation exchange reactions, but nitrate ions are readily leached from the soil while phosphate ions are largely retained. The soil mechanisms responsible for phosphorus retention are discussed in this module.

Phosphorus Behavior in Terrestrial Systems

Figure 1 shows a general scheme for phosphorus relations in a land application system. Waste inputs of phosphorus occur in both organic and inorganic forms. Organic forms predominate in sludges and manures while inorganic forms are more prevalent in wastewater effluents. Various forms occur in the soil including phosphorus bound in organic matter, largely humus, dissolved phosphorus in the soil solution, and phosphorus bound in inorganic forms. Both freshly added and native organic forms are slowly mineralized by soil microorganisms through normal decomposition processes (1) (Numbers refer to Figure 1). Some of this mineralized P may be reabsorbed and thus temporarily immobilized by the microbes (2). Immobilization is most significant immediately following waste application when the microbial population is rapidly increasing. Dissolved P comprises only a small fraction of the total soil phosphorus. Nevertheless, it is from this fraction in the soil solution that plants obtain needed phosphorus for growth and development (3), and from which any leaching loss occurs. Dissolved P is in equilibrium with the much larger amount of phosphorus bound in inorganic forms (4), primarily iron-, aluminum-, and calcium-phosphates. The equilibrium relationship between these forms and dissolved P is of considerable importance in the overall performance of a land treatment system.

Phosphorus occurs in the soil in several forms-it is bound in organic matter, dissolved in the soil solution and bound in inorganic forms.

Plants obtain the necessary phosphorus for growth and development from dissolved P which comprises only a small fraction of the total phosphorus in soil. Any leaching loss also occurs from dissolved phosphorus.

Phosphorus in Wastes Comes from Several Sources

Phosphorus in wastes arises from a variety of sources. Organic forms occur in microbial tissue, plant residues, and metabolic by-products from living organisms. Inorganic forms exist as condensed

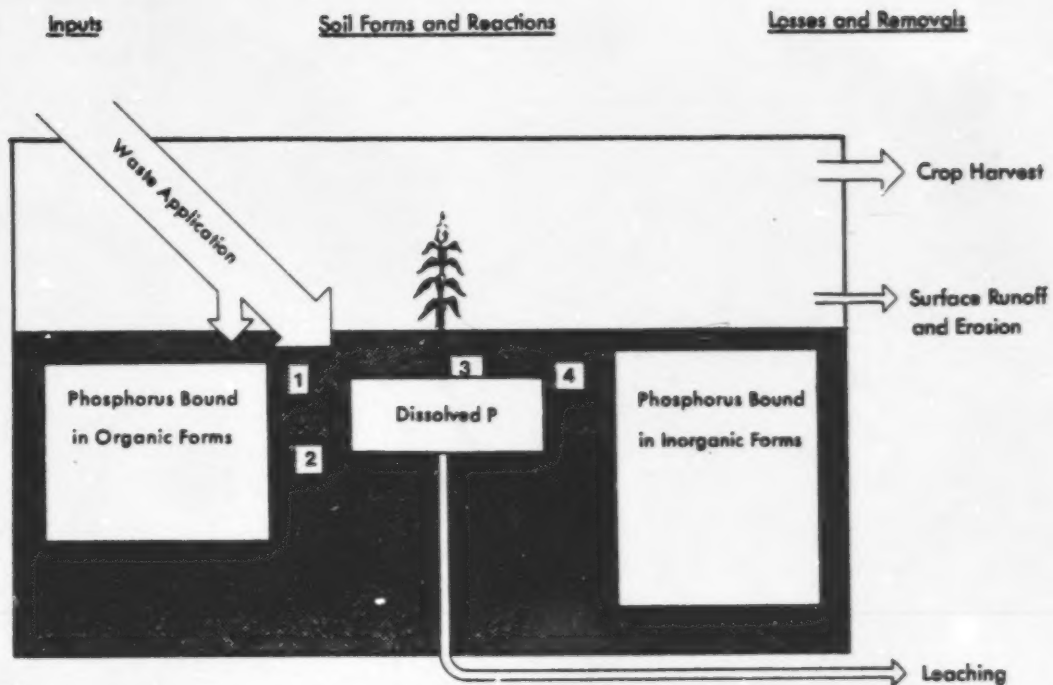


Figure 1. Phosphorus additions to soil are largely held either in organic combination or by reaction with soil minerals. Dissolved phosphorus, in equilibrium with bound forms, supplies plant needs and is subject to leaching.

phosphates from detergent residues, and as ortho-phosphate anions (H_2PO_4^- , HPO_4^{2-}). Most wastes, however, are characterized in terms of total P without further distinction. Some representative values for different wastes along with common loadings to land are listed in Table 1.

Organic phosphorus found in waste comes from microbial tissue, plant residues, and metabolic by-products of living organisms; inorganic phosphates arise from detergent residues, fertilizers, etc.

TABLE 1. Total phosphorus content in various wastes and common annual loading to land.

Waste	Total P	Annual P loading to land	
	mg P/l	Assume 10 mg P/l	
		Low rate ¹	High rate ²
Sewage Effluent		- - - lb/acre-yr - - -	
Untreated	6-20		
Primary	8-14	135	1420
Secondary	4-17		
		Assume 3% P (dry wt.) ³	
Sewage Sludge	1 - 6% (dry wt.)	270	

¹ Assumes application rate of 2"/week for 30-week period (representative of irrigation and overland flow systems)

² Assumes application rate of 6"/day for 14 days followed by 14-day rest period over a 30-week season (representative of rapid infiltration system)

³ Assumes one annual application of liquid sewage sludge (96% moisture; 4% solids) in amount of one acre-inch

Sources: Keeney et al. 1975; Peterson et al. 1973; Pound and Crites 1973a; Reed et al. 1972.

Figure 2 assigns expected values for the input and output terms of the P balance through a crop irrigation system, using a typical application schedule of 2 inches/week for a 30-week season. The influent concentration of 10 mg/l as P is an average value for raw domestic wastewater and primary or secondary effluent, and is

suitable for these demonstration purposes. As in any characterization of waste inputs to land treatment, laboratory studies would be performed on the specific influent to be treated.

MASS TRANSFER OF PHOSPHORUS

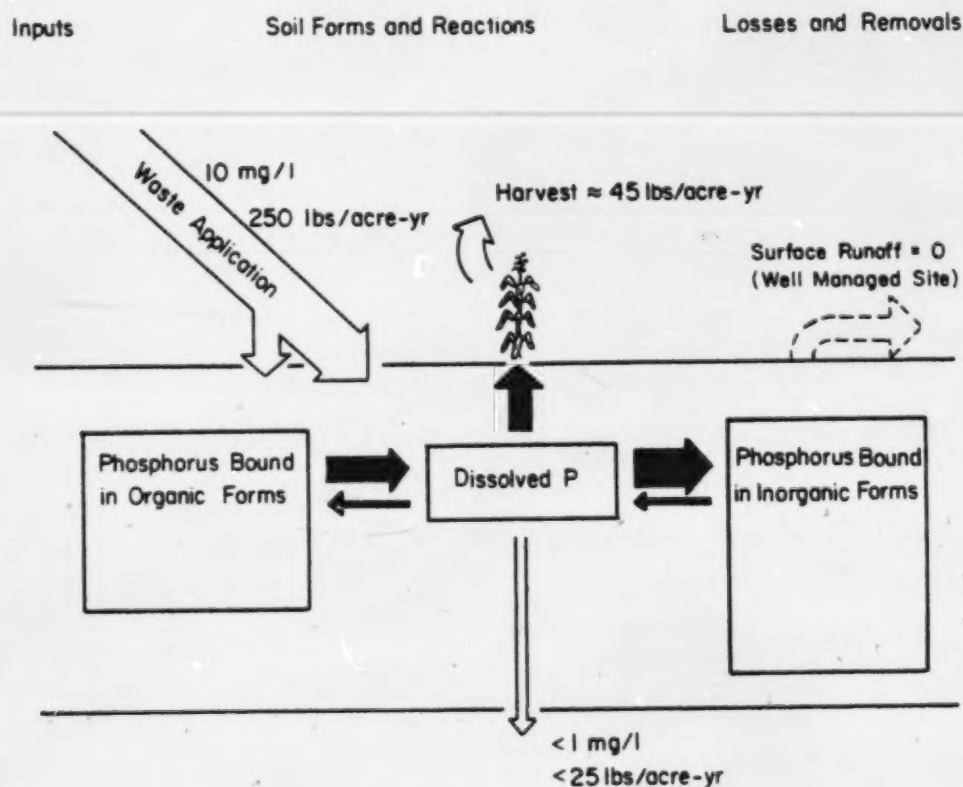


Figure 2. Mass flow diagram shows P concentration and mass interactions which could be expected at typical loading rates.

Soil Retains Phosphorus by Adsorption, Precipitation

Unlike nitrogen, phosphate anions are largely retained in the soil through specific adsorption and precipitation reactions. Both reactions were introduced in general terms in Module 3 "Soil as a Treatment Medium". The particular type of reaction and the end products formed, however, are dependent on the mineralogical composition of the soil medium, the pH of the soil solution, and the residence time of phosphorus in the soil.

Phosphate anions are retained in the soil by specific adsorption and precipitation reactions.

Fine Textured Soils Retain Phosphates Better

Fine textured soils in general have a greater capability to retain phosphates than do soils of coarser texture. Texture alone, however, does not describe the actual mineralogical composition of the clay fraction. Of primary interest are the iron (Fe), aluminum (Al), and calcium (Ca) bearing minerals since they are highly instrumental in phosphorus reactions. The principal iron and aluminum minerals are the hydrous oxides such as gibbsite, goethite, and limonite; principal calcium minerals are the various forms of apatite, and calcium carbonate (calcite).

Fine textured soils generally retain phosphorus to a greater extent than coarse soils do.

Form of Phosphorus and Its Retention Vary with pH

Figure 3 shows the general relationships between soil pH and phosphorus reactions. The form of phosphorus in solution is determined by pH. In the acid range H_2PO_4^- predominates, while in the alkaline range HPO_4^{2-} is more abundant. A mixture of the two forms occurs around neutrality (pH 7). The actual mechanisms for phosphate retention are also a function of pH. In the very acid range (pH < 5), the solubility of iron and aluminum increases. Some soluble phosphate then reacts with the iron and aluminum to form insoluble precipitates (A) (letters refer to Figure 3). Much larger quantities of phosphate are

The pH of the soil determines the form of phosphorus in solution and the way it will be retained.

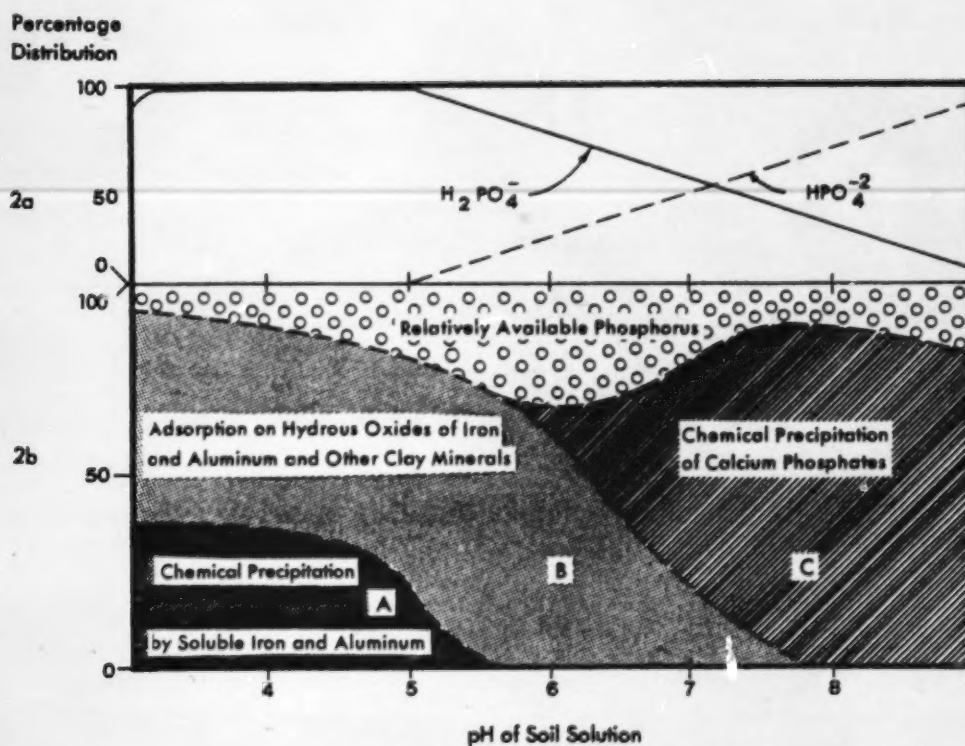


Figure 3. Forms of dissolved phosphorus (3a) and phosphorus retention mechanisms (3b) vary with pH. In the acid range, phosphates are bound with iron and aluminum compounds (A,B) while in the alkaline range, calcium phosphates predominate (C). Maximum availability of phosphorus for plant uptake as well as leaching occurs between pH 6 and 7. (adapted from Brady, 1974).

adsorbed onto iron and aluminum hydrous oxides (B), and this occurs over a wide pH range. Additional adsorption occurs on other clay minerals. Precipitation of insoluble calcium phosphates begins at a pH of around 6. As pH increases further, reactions with calcium become the dominant mechanism for P removal (C). Thus, some mechanism for efficient phosphorus removal functions over a wide range of soil pH values.

Efficient phosphorus removal mechanisms function over a wide range of pH values.

At the top of Figure 3b is an area termed "relatively available phosphorus". This refers primarily to the availability to plants, but also indicates the availability for leaching from the soil. Maximum availability exists over the pH range of 6 - 7. From the standpoint of phosphorus retention, it would seem advantageous to maintain a pH of less than 6 or perhaps around 8. This would be true if phosphorus were the only waste constituent of concern; however, other factors must also be considered. For example, heavy metals are less firmly held in acid soils and are thus more likely to move into the drainage water. See Module 11, "Potentially Toxic Elements", for discussion of this point. This can be minimized by maintaining a pH value at or above neutrality. In addition, microbial activity generally increases in neutral to alkaline soils, and thus decomposition of organic wastes is more rapid in this pH range. Moreover, plant requirements for various nutrients are more apt to be met in the mid-range of pH values. Thus, while it is true that acid soils have a large capacity to retain P, there are other reasons to favor a higher pH environment. Many wastewaters themselves have a pH of around 7 and repeated applications of such water tend to raise the pH of an initially acid soil.

Although acid soils are most favorable for retaining phosphorus, other factors must be considered when deciding on the most favorable pH for the site, including the retention of potentially toxic elements, microbial activity, and availability of nutrients to plants.

Availability of Phosphorus in Soil Depends on Residence Time

Although Figure 3 indicates the compounds formed in soil, it oversimplifies the actual dynamics of reaction. The availability of phosphorus compounds in soil is highly dependent on time. Equilibria between adsorbed and precipitated forms and those in solution may be established within a few hours after addition of wastewater. However, readjustments occur over periods of weeks, months or longer, resulting in the formation of even more insoluble forms. A schematic of this concept is presented in Figure 4.

Within the soil, dissolved phosphorus is in equilibrium with loosely adsorbed materials and/or the more soluble precipitates. These loosely bound forms are termed labile P and will readily dissolve should the solution P concentration decrease due to either plant and microbial uptake or dilution with rainwater. Likewise, if the solution P concentration should increase, as with wastewater additions, P would initially move from the soil solution into the labile reserve.

Moving downward in the diagram, successive boxes represent more insoluble or more tightly adsorbed forms, often said to be "fixed". Conversion to these less available forms takes place much more slowly than changes between the dissolved and labile forms.

Formation of compounds in the lower categories is not well understood. In the case of the iron and aluminum hydrous oxides, fixation is thought to involve a diffusion of phosphorus deeper into the mineral itself thus rendering the P less available. Calcium phosphates in the least soluble range apparently arise from dissociation-reprecipitation reactions.

Availability of phosphorus compounds in soil varies over time. Readjustments occurring over periods of weeks, months, or longer result in the formation of more insoluble forms.

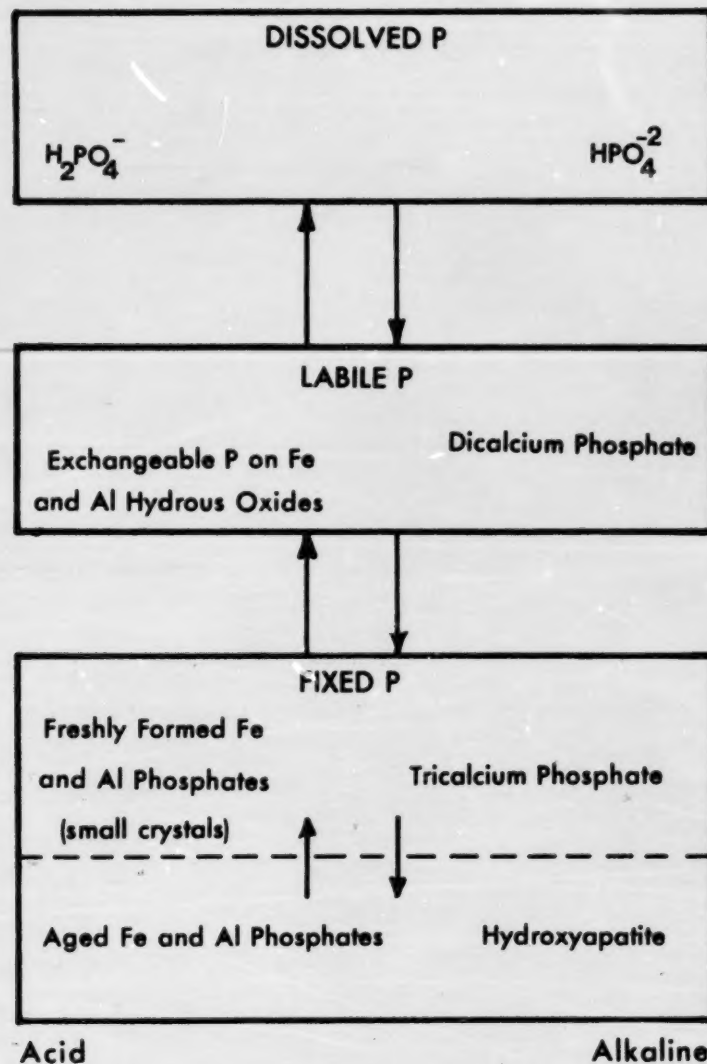


FIGURE 4. Phosphorus compounds in soil can be classed in three general groups according to their availability both for plant uptake and for leaching. Highly available dissolved P is in equilibrium with less available labile P which in turn is in equilibrium with essentially unavailable fixed forms. At any given time, most soil phosphorus, perhaps 80 - 90%, occurs in a fixed form.

The differences in availability of calcium phosphates are indicated by their solubility product constants (K_{sp}). As described in Module 3 "Soil as a Treatment Medium", a solubility product constant is obtained by multiplying together the concentrations of reactants (moles/l) in a saturated solution. The smaller the K_{sp} value for a given compound, the more insoluble it is. K_{sp} values for the insoluble calcium phosphates presented in Figure 4 are as follows:

Compound	Chemical Formula	Solubility Product (K_{sp})
Dicalcium phosphate	CaHPO_4	2.8×10^{-7}
Tricalcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$	1.0×10^{-27}
Hydroxyapatite	$3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$	2.0×10^{-114}

Comparison of these values indicates the extreme insolubility and thus the high degree of fixation which occurs in the aged calcium compounds.

Phosphorus must remain in the soil for periods ranging from weeks to years for these least available compounds to form. With continuous applications of wastewater, residence time does not permit such formation in many cases. For this reason, resting periods between applications will generally increase the lifetime of the system in terms of phosphorus retention capabilities.

Heavy applications of wastewater not only decrease the residence time in the soil, but also increase the chance of soil saturation with water, producing anaerobic conditions. Under such conditions, iron changes from the ferric ion to the ferrous ion. This change increases phosphate solubility, reduces P retention, and may even release previously fixed P to the soil solution. Thus, it is important to keep the soil well aerated if it is to be an effective phosphorus sink.

The aged calcium compounds are the least soluble form of phosphorus and have the highest degree of fixation; at any given time most soil phosphorus occurs in fixed form, perhaps 80 to 90%.

Continuous applications of wastewater prevent the formation of the most insoluble compounds; resting periods between applications increase the lifetime of the site in terms of phosphorus retention.

Soil must be kept well-aerated to function as an effective phosphorus sink.

Phosphorus may be removed from the site by various means

The principal pathways for loss or removal of phosphorus are surface runoff and erosion, crop harvest, and leaching. Loss via surface runoff would be highly variable from one site to another depending on natural precipitation, topography, season, and application rates and methods. As recommended in Module 8, "Climate and Wastewater Storage" a land treatment site should be designed to contain the flow from a 25-year, 24-hour storm with no surface runoff outside the site boundaries. Minimizing surface runoff simultaneously minimizes erosion. Since erosion is the only way that fixed phosphorus is lost, its control is very important.

Because fixed phosphorus is only lost through soil erosion, surface runoff control is effective in minimizing this loss.

Table 2. Phosphorus removal by selected crops when irrigated with municipal sewage effluent.

Crop	Yield per acre	P Removal lb/acre-yr
Corn Grain	114 bu	26
Corn Silage	6.0 tons	43
Wheat Grain	54 bu.	20
Reed Canarygrass (3 cuttings)	4.3-7.0 tons	33-56

Sources: Sopper and Kardos 1973; Kardos et al. 1974.

Crop uptake of phosphorus is rather low in contrast in nitrogen. A few representative values are presented in Table 2. Nevertheless, crop uptake can account for a significant portion of applied phosphorus under low-rate loading conditions (135 lb P/acre-yr as given in Table 1). Under high-rate conditions, crop uptake, even though remaining the same in lb/acre-yr, would reflect a much lower percentage of applied P. Vegetative cover, however, is important for other reasons including erosion control and maintenance of infiltration. Moreover, transpiration

by plant cover reduces leaching and thus increases the residence time of wastewater phosphorus in the soil. The overall significance of a cover crop is thus magnified.

Leaching losses of phosphorus are very small in natural systems. Inputs of wastewater or sludge need not result in excess P leaching since the fixing power of many soils is quite high. Nevertheless, careful management is necessary to prolong the life of the system. Coarse sandy or gravelly soils have a high hydraulic loading potential, but often only limited ability to retain phosphorus. Moreover, since water moves readily, such soils may not wet uniformly and thus the P fixation will be further reduced. A short residence time will also reduce fixation since formation of the more insoluble compounds is precluded.

Phosphorus Retention of the Soil Can be Assessed

When wastewater is applied to a soil, initial reactions occur in the surface layer. The phosphorus concentration in the water moving out of this layer will be reduced in accordance with the amount retained. Sequential changes in P concentration at various soil depths in response to repeated wastewater applications are illustrated in Figure 5.

In the initial condition prior to wastewater additions, the native fraction of bound phosphorus in many soils is sufficient to produce P concentrations in the soil solution of 5 - 250 ppb (parts per billion) (Taylor and Kunishi, 1974). As wastewater is applied, the phosphorus concentration in the surface layer will increase and water of steadily decreasing concentration will move into lower layers. Continued application results in the gradual saturation of soil layers from the surface downward. Different soil

Keeping the hydraulic loading rate low enables crops to take up a considerable portion of the phosphorus applied plus yielding other benefits.

Leaching loss of phosphorus can be kept to a minimum through careful management of the land treatment site. Special care must be taken with coarse soils.

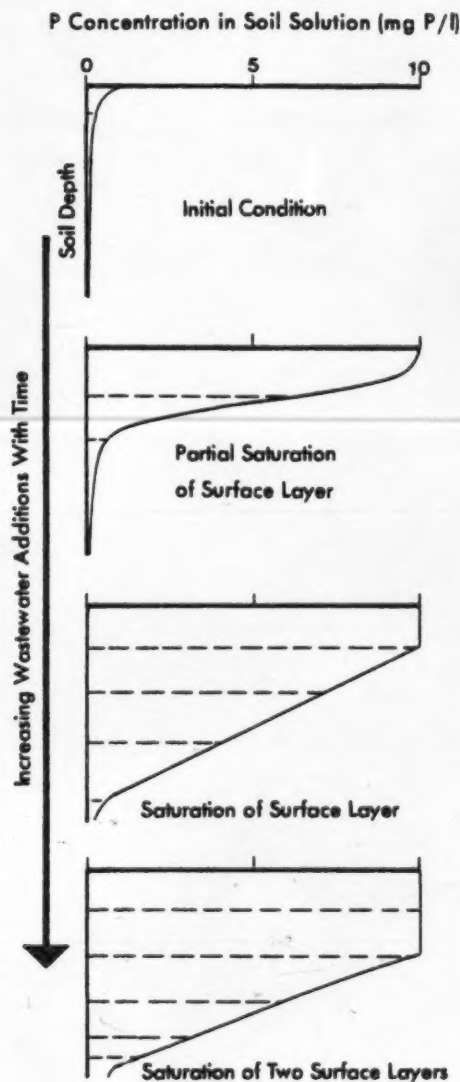


Figure 5. Dissolved phosphorus concentration in most unamended soils is less than 1 mg/l. Initial additions of wastewater (10 mg P/l) cause a readjustment in the equilibrium between dissolved and bound phosphorus in the surface soil layer. As more and more phosphorus is applied and retained, successive soil layers become saturated; at this point, the phosphorus concentration in the soil solution equals that of the wastewater itself. The time required for saturation of any given layer(s) varies from a few weeks to several decades depending on soil characteristics and wastewater application rates. (after Taylor and Kunishi, 1974).

layers, however, will have different capacities to retain phosphorus. Therefore, in the case depicted at the bottom of Figure 5, the two saturated layers could contain considerably different amounts of phosphorus, instead of equal concentrations as shown.

There is no simple method to determine the amount of phosphorus which a soil can retain before saturation. Some indication, however, is obtained by so-called adsorption isotherms, which describe the relationship between that quantity of phosphorus held in the soil and that remaining in the soil solution (Ellis, 1973; Powers *et al.*, 1975; Taylor and Kunishi, 1974). To construct an adsorption isotherm, soil samples from a given layer are combined with a series of solutions containing known amounts of phosphorus. After initial equilibrium is reached (12-18 hours), the solution is analyzed; the difference between initial and final phosphorus concentrations indicates the amount retained. When data from several such trials are plotted, the resulting curves quantitatively describe the relationship between adsorbed and dissolved phosphorus.

Adsorption isotherms help indicate the amount of phosphorus which a soil can retain.

Sample adsorption isotherms for two different soil layers are shown in Figure 6. The horizontal axis represents the P concentration in solution in equilibrium; the vertical axis indicates the corresponding amount of P retained by the soil. Suppose a wastewater containing 10 mg P/l is applied to a sample from the soil layer described by isotherm A. As the first wastewater is added, this soil layer will transmit solution containing less than 0.3 mg P/l until approximately 145 mg P/kg of soil have been retained. Phosphorus retention is then equivalent to about 42 lb/acre-inch of soil, assuming a soil bulk density of 1.3 g/cm^3 . With continued application,

the P concentration in the water passing out of this layer will slowly rise to the 10 mg/l level of the wastewater itself. At this point, the soil is saturated and as defined by the adsorption isotherm, will contain approximately 700 mg P/kg or 200 lb P/acre-inch. In contrast, the soil described by isotherm B has much lower retention capacity and at saturation will contain only about 29 lb P/acre-inch (100 mg P/kg of soil).

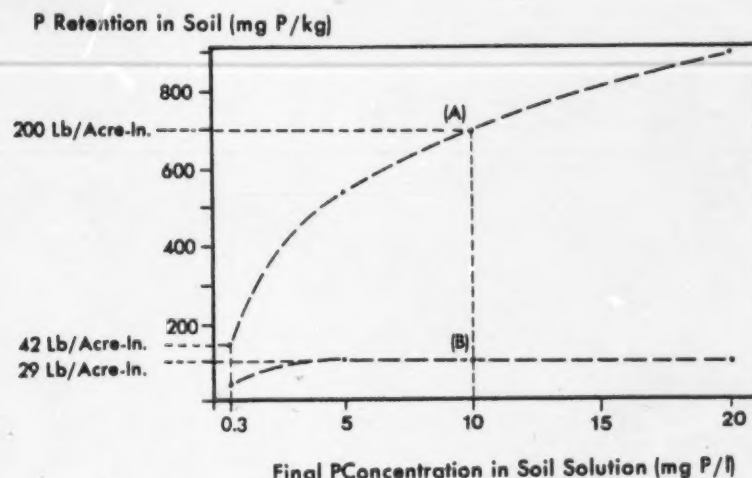


FIGURE 6. Adsorption isotherms for two different soil layers indicated a wide variation in Pretention capabilities. Such analyses are useful to show relative differences within and among soils; however, isotherms provide conservative estimates since they do not account for the slower reversion-type reactions. (after Taylor and Kunishi, 1974)

Table 3 presents phosphorus retention capacities for several Michigan soils as predicted by adsorption isotherms. Note the variation within as well as among the different soils. Although phosphorus retention is often reflected by texture, the variation shown in these soils is not necessarily attributable to textural differences. The dune sand clearly shows the least overall ability to retain phosphorus, and the sand and gravel layer in the Kalamazoo loam shows the lowest retention of any single layer. The highest retention, however, occurs in the Rubicon sand, even greater than the silty clay layers on the Ontonagon series. This is due to appreciable amounts of iron and aluminum within the Rubicon sand profile. All sands are obviously not comparable in this respect.

TABLE 3. Phosphorus retention capacity in selected soils as predicted by adsorption isotherms.

Soil type	Textural class by layer	Depth	Phosphorus retention capacity	Retention capacity to 48 inches
		inches	lb/acre-ft	lb/acre
uniform dune sand	sand	0-60	77	308
Spinks loamy sand	loamy sand	0-20	360	1809
	loamy sand	20-50	518	
	sand	50-60	277	
	loam	0-12	340	
Kalamazoo loam	sandy clay loam	12-36	908	2173
	sand & gravel	36-60	17	
	loam	0-12	791	
Miami loam	clay loam	12-30	546	2786
	loam	30-60	784	
Rubicon sand	sand	0-12	455	3437
	sand	12-24	1524	
	sand	24-60	729	
Ontonagon silty clay loam	silty clay loam	0-12	1337	4240
	silty clay	12-36	1160	
	silty clay	36-60	583	

Source: Schneider and Erickson 1972.

It should be emphasized that adsorption isotherms give only a partial indication of phosphorus retention since they do not account for the slow, yet very important, reversion-type reactions that occur in soils over time. Nevertheless, the data in Table 3 indicate minimum site lifetimes ranging from 13 to 30 years for low-rate applications of domestic sewage effluent. For example, assuming a wastewater with 10 mg P/l applied at a rate of 2 inches/week for 30 weeks (135 lb/acre-yr), four feet of Rubicon sand would take over 25 years to reach phosphorus saturation. Reversion reactions would further prolong the useful lifetime of the site. In contrast, adsorption isotherms indicate only a limited site lifetime where application rates are employed as in rapid infiltration systems. An annual phosphorus application of 1500 lb/acre would seemingly saturate the same depth of Rubicon sand in less than three years. Alternate wetting and drying cycles, however, may allow for considerable reversion reactions so that the actual phosphorus retention would be greater. Under such circumstances, actual on-site demonstrations are necessary to fully determine the effectiveness of soil in phosphorus removal.

Because adsorption isotherms do not show the slow, reversion type reactions that occur in soils over time, they give only a partial indication of phosphorus retention.

Alternate wetting and drying cycles allow for reversion reactions, increasing the phosphorus retention of the soil.

Experience With Phosphorus in Existing Systems

Irrigation Systems Can Almost Completely Remove Phosphorus

Existing crop irrigation systems, where wastewater applications range from 1 to 3 inches per week, generally show nearly complete removal of phosphorus. Table 4 shows data based on 11 years of effluent irrigation in the Pennsylvania State University Wastewater Renovation and Conservation Project. Over these years, no site has shown leaching losses greater than 3% of the total phosphorus applied (Kardos and Hook, 1976).

Crop irrigation systems of land treatment that apply 1 to 3 inches per week show almost complete removal of phosphorus.

TABLE 4. Approximate phosphorus balance for an 11-year period (1963-1973) of effluent irrigation on the Penn. State Wastewater Renovation and Conservation Project.

Vegetative cover	Total P applied	Removal by harvest	Est. loss to drainage	Soil retention
- - - - - lb/acre - - - - -				
Corn ¹	706	309	6	391
Reed canarygrass	1975	438	12	1525
Abandoned field (white spruce and herbaceous species)	931	0	31	900
Hardwood forest	1611	0	18	1530

¹ Corn, reed canarygrass, and abandoned field areas were all on Hublersburg clay loam soil; hardwood forest was on Morrison sandy loam soil.

Source: Kardos and Hook 1976.

Roughly comparable results are reported at a sewage farm in the Netherlands, where untreated sewage effluent has been applied to a sandy soil for over 50 years. Application rates have ranged from 6 to 14 inches per month. Fifty-year totals (Table 5) indicate nearly 93% combined phosphorus removal by crops and soil to a depth of 2.6

feet (Beek and deHaan, 1974). Major retention of phosphorus in the surface soil layers is indicated by present distribution as shown in Figure 7. Note the similarity of this data to the general concept depicted in Figure 5.

Table 5. Approximate phosphorus balance for a 50-year period on a 247-acre sewage farm in the Netherlands.

Total P applied	Harvest removals (hay, milk, meat)	Estimated Loss by Leaching	Soil Retention in 2.6 ft.
-----lb/acre-----			
8400	779 (10.5%)	390 (5.3%)	6115 (82.6%)

Source: Beek and deHaan, 1974.

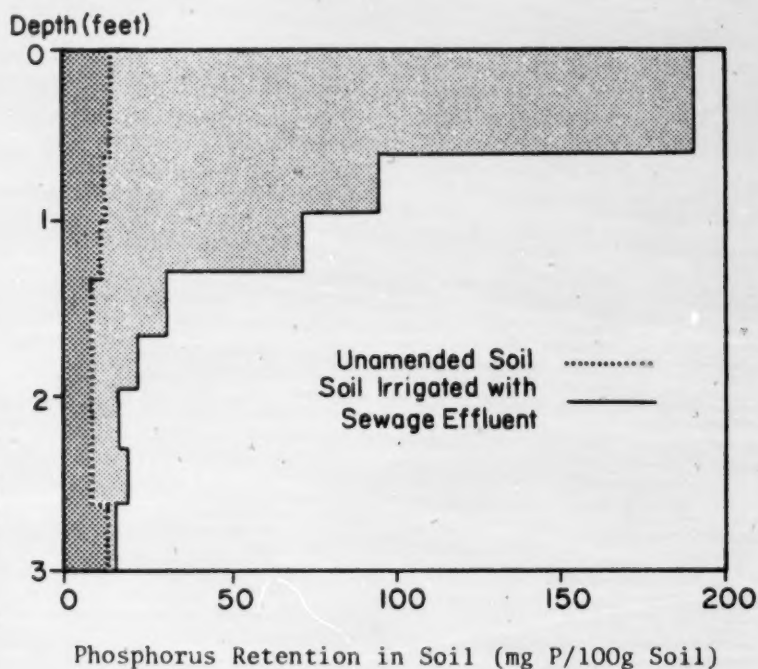


FIGURE 7. Distribution of phosphorus with depth in a sandy soil profile after 50 years of irrigation with untreated sewage effluent. The difference between amended and unamended profiles indicates that over 80% of the applied phosphorus is held in the upper 2.6 feet of soil (after Beek and deHaan, 1974).

Overland Flow is Less Effective in Phosphorus Removal

Currently operating overland flow sites are often less effective in phosphorus removal than irrigation systems. Percent renovation values of 50% and 35% have been reported for systems at Ada, Oklahoma, and Melbourne, Australia respectively (EPA, 1975). The surface flow path on overland flow sites does not provide much opportunity for contact with soil particles except at the immediate ground surface. A few inches of permeable topsoil overlaying nearly impermeable subsoil, however, can increase the contact by allowing for subsurface flow within this upper layer. The more contact with soil particles, the greater the opportunity for renovation. Resting periods can also increase P renovation in the overland flow approach. At the Campbell Soup facility at Paris, Texas, adoption of an intermittent application schedule increased P removal from 50% to nearly 90% (Gilde *et al.*, 1971).

Although overland flow systems are less effective in phosphorus removal than irrigation, removal can be increased by overlaying impermeable subsoil with a few inches of permeable topsoil to increase wastewater contact with soil particles.

Rapid Infiltration is the Least Effective in Phosphorus Removal

Rapid infiltration systems provide the least opportunity for phosphorus renovation of any land application method. Nevertheless, these systems vary considerably because of different phosphorus loading rates and the nature of the receiving soil.

The Flushing Meadows project near Phoenix, Arizona exemplifies the upper extreme in phosphorus loading. Wastewater applications in excess of 300 acre-feet/yr with initial P concentrations ranging from 7-12 mg/l produce an annual phosphorus loading of between 5700 and 9800 lb/acre. Moreover, the coarse soil, a loamy sand overlying deep sand and gravel deposits, contains only small amounts of phosphate-fixing minerals such as iron or aluminum oxides. A static water table exists at about 10 feet.

Rapid infiltration systems are the least effective form of land treatment in terms of phosphorus removal, but the success of systems varies depending on the rate of phosphorus loading and the nature of the receiving soil.

Not surprisingly, phosphorus removal is relatively low. Samples from a 30-foot well (i.e. 20 feet below the water table), have shown phosphorus concentrations of 5 mg/l (Bouwer, 1973). Estimates of the respective roles of soil retention and groundwater dilution in reducing phosphorus concentrations are not available.

In contrast, deep sand beds at Lake George, New York seem to provide considerable renovation of wastewater phosphorus under applications ranging from approximately 65 to 100 acre-ft/yr. (Pound and Crites, 1973b; Aulenbach et al., 1975). Initial phosphorus concentrations in the wastewater, however, are low (1 - 4 mg P/l) so that annual P loading ranges from 175 to 1080 lb/acre, far less than at Flushing Meadows. Here again, the effect of groundwater dilution complicates any specific analysis of phosphorus removal by the soil.

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PHOSPHORUS CONSIDERATIONS

Objectives

Upon completion of this module, the participant should be able to:

1. Describe common loading rates of phosphorus in land application systems and where the various forms of phosphorus found in wastewater come from.
2. Describe those soil conditions which favor the retention of phosphorus.
3. Discuss the availability of phosphorus in the soil and how phosphorus is retained in the soil in various forms.
4. Discuss how the land application site should be managed to enhance phosphorus removal.
5. Discuss the relative effectiveness of spray irrigation, overland flow, and rapid infiltration systems for phosphorus removal.

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PHOSPHORUS CONSIDERATIONS

Module 19

January, 1978

PHOSPHORUS CONSIDERATIONS

This module is the level II consideration of Phosphorus (Slide 1). Phosphorus, like nitrogen, is an essential nutrient for the growth of plants and animals. It is usually considered the limiting nutrient for plant growth in surface waters, thus its discharge is often considered the major cause of eutrophication in rivers and streams. This pond in Slide 2 suffers from an excess of phosphorus.

Phosphorus and nitrogen differ in their behavior in the soil. Notice in Slide 3 the possible fate of the two nutrients in a land treatment system. This module considers the soil mechanisms responsible for the treatment of phosphorus and the possible loading rates for phosphorus.

The objectives for this module are located in an envelope that was with this lesson (Slide 4). The envelope is labelled "Objectives". Stop the recorder and read the objectives for this tape.

Slide 5 indicates the mass flow for phosphorus when it is applied with a two inch per week irrigation of raw wastewater. The phosphorus in municipal wastes is bound mainly in inorganic forms with a lesser portion of it being organic. This latter portion along with the native organic forms, is slowly mineralized by soil microorganisms through normal decomposition processes as depicted in Slide 6. Some of the mineralized P may be reabsorbed and thus temporarily immobilized by the microbes. This immobilization is most significant immediately following waste application when the microbial population is rapidly expanding. The dissolved phosphorus in the soil comprises only a small fraction of the total soil phosphorus seen in Slide 7. Nevertheless, it is from this fraction in the soil solution that plants obtain needed phosphorus for growth and development, and from which any leaching loss occurs. The phosphorus in solution is in equilibrium with the much larger amount of phosphorus bound in inorganic forms, (Slide 8) primarily iron, aluminum and calcium phosphates. The equilibrium relationship between these forms and dissolved P is of considerable importance in the overall performance of a land treatment system.

Phosphorus in wastes comes from a variety of sources (Slide 9). Organic forms occur in microbial tissue, plant residues and metabolic by-products from living organisms. Inorganic forms exist as condensed phosphates from detergent residues and as orthophosphate anions. Most wastes, however, are

characterized in terms of total P without further distinction. Slide 10 shows some typical levels of phosphorus in effluents and common loading rates for a thirty week period.

Unlike nitrogen, phosphate anions are largely retained in the soil through specific adsorption and precipitation reactions (Slide 11). Both of these reactions were introduced in general terms in Module #3, "Soil as a Treatment Medium". The three variables that define the reactions are indicated in Slide 12. They will be considered individually.

The mineralogy of a site is of prime importance for the binding of phosphates. Fine textured soils, in general, have a greater capability to retain phosphates than do soils of coarser texture. This is because the essential minerals shown in Slide 13 - iron, aluminum, and their hydrous oxides, and calcium, are generally found in greater concentrations in the clays. There are some sands, however, that have relatively high concentrations of these elements to effectively bind a great amount of the phosphates.

The pH of the soil affects both the form of phosphorus in solution and the actual mechanisms for phosphate retention. Notice in Slide 14 that the concentrations of the two anions vary as the pH goes from acid to basic. A mixture of the two forms occurs around neutrality. This indicates the actual mechanisms for phosphate retention. In very acid conditions the solubility of iron and aluminum increases (Slide 15). Some of the soluble phosphates already in solution, can then react with these to form insoluble precipitates. Over a much wider pH range the phosphates are adsorbed onto the iron and aluminum hydrous oxides and other clay minerals (Slide 16). Around neutrality chemical precipitation of calcium phosphates begins, and becomes dominant as the pH increases (Slide 17). Thus there is some mechanism for efficient phosphorus removal over a wide range of soil pH's.

Notice the percentage of phosphorus that is available. This phosphorus is available for absorption by plants but also for leaching from the soil. It can be seen that if phosphorus considerations were the only considerations in land application, it would be advantageous to maintain the pH well below six or around eight. Other factors, however, must also be considered. Slide 18 indicates a number of considerations that must be given when considering the pH of a land application site. The width of the band varies directly with the increase in the parameter indicated. When treating for a specific characteristic of the waste, the pH can be adjusted accordingly, to maximize treatment. The affect of this pH adjustment, however, on other aspects of the waste treatment

must also be considered. Wastewater generally is in the neutral range and maintaining a pH other than neutral may present a continuing problem.

Equilibria between adsorbed and precipitated forms of phosphorus and that in solution may be established within a few hours after addition of wastewater (Slide 19). Readjustments occur, however, over periods of weeks, months, or longer, resulting in the formation of even more insoluble forms. This schematic in Slide 20 indicates these readjustments.

The loosely adsorbed material and the more soluble precipitates, called labile phosphorus will readily dissolve should the solution P concentration decrease due to either plant and microbial uptake or dilution with rainwater. Should the solution phosphorus concentration increase, the tendency would be for the labile reserve to increase.

Moving downward in the diagram, successive boxes represent more insoluble or more tightly sorbed forms, often said to be fixed. Conversion to these less available forms takes place much more slowly than changes between the dissolved and labile forms.

The difference in availability of calcium phosphates is indicated by their solubility product constants. This is obtained by multiplying together the concentrations of reactants, in moles per liter, in a saturated solution. The smaller the solubility product, the more insoluble the compound. Notice in Slide 21, the extreme insolubility and thus the high degree of fixation of the phosphate.

The more unavailable forms of phosphorus may take weeks to years to form. With continuous applications of wastewater, residence time does not permit such formation in many cases. Resting periods will generally increase the residence time of phosphorus and consequently the lifetime of a site in terms of phosphorus retention (Slide 22).

Saturation of the soil by water affects phosphorus retention in two ways (Slide 23). First, there is just more water available for leaching to groundwater. Second, anaerobic conditions, which are caused by the saturation, changes iron from the ferric to the ferrous ion form. This increases the phosphate solubility, reduces the phosphorus retention, and may even release previously fixed phosphorus to the soil solution. For further information on soil saturation, see Module 3, "Soil as a Treatment Medium" and Module 8, "Climate and Wastewater Storage" (Slide 24).

(Slide 25) The possible pathways of loss or removal of any material from a land application site are through runoff, erosion, crop harvest, and leaching (Slide 26). In a well managed and designed site, there should be little if any runoff and consequent erosion.

As Slide 27 indicates, crop uptake of phosphorus is rather low. It does, however, account for a significant portion of the phosphorus applied in a low rate system. Vegetative cover is important for other reasons including maintenance of the infiltration rate, erosion control, and through transpiration, control of leaching. Thus the significance of a cover crop is magnified beyond its uptake of phosphorus. For further information on the value of a crop, see Module 7 "The Role of Vegetative Cover" (Slide 28).

Inputs of wastewater or sludge need not result in excess phosphorus leaching since the fixing power of many soils is quite high (Slide 29). The soils used in most high rate systems, however, may have only limited ability to retain phosphorus because of their mineralogy and because of a lack of uniform wetting and brief wastewater residence time. Even so, seventy percent or more of the phosphorus may be removed from the effluent.

When wastewater is applied to a soil, initial reactions occur in the surface layer. The phosphorus concentration in the waste moving out of this layer will be reduced in accordance with the amount retained. As Slide 30 indicates, when wastewater is first applied the phosphorus status of the surface layer will increase and water of steadily decreasing concentration will move into lower layers, shown in Slide 31. Continued application results in the gradual saturation of soil layers from the surface downward, shown in Slide 32. As saturation is approached the phosphorus concentration in the soil solution passing to the lower layers will increase. At saturation, concentration of phosphorus in the soil solution passing through a layer will equal the concentration in the wastewater applied as in Slide 33. Different soil layers, however, will have different capacities to retain phosphorus. Therefore, the two saturated layers depicted in this slide may contain considerably different amounts of phosphorus.

There is no simple method to determine the amount of phosphorus which a soil can retain before saturation. One method of dealing with the phosphorus loading is to examine the history of sites where phosphorus application has been ongoing for several years (Slide 34).

Existing crop irrigation systems, where wastewater applications range from one to three inches per week, generally show nearly complete removal of phosphorus shown in Slide 35. This slide shows data based on eleven years of effluent irrigation in the Pennsylvania State University wastewater renovation and conservation project. Over these years, no site has shown leaching losses greater than three percent of the total phosphorus applied. Even when liquid digested sludge was added to the wastewater bringing the phosphorus concentration up to 20 to 25 milligrams per liter and applying three inches per week, there was essentially complete removal, seen in Slide 36.

Slide 37 indicates roughly comparable results with nearly 93% removal in only the top 2 1/2 feet. This is after 50 years of application of untreated sewage at rates ranging from 6 to 14 inches per month. Major retention of phosphorus in the surface soil layers is indicated by present distribution as indicated in Slide 38. Note the similarity of this data to the general concept of soil saturation of phosphorus indicated earlier.

The systems quoted above are irrigation systems. Currently operating overland flow (Slide 39) and rapid infiltration sites are generally less effective at treating phosphorus. Slide 40 indicates representative data from these two treatment methods. The surface flow path on overland flow sites, does not provide much opportunity for contact with soil particles. And, of course, the rapid infiltration sites have the least total contact time. The essential ingredient, however, for phosphorus retention in the soil seems to be a resting period of at least 2 days between applications. The systems indicated in Slide 40 that provided at least that amount of rest period has phosphorus renovation efficiencies of greater than 60%, using either of the application methods (Slide 41).

In summary, the treatment of phosphorus involves both chemical and biological mechanisms as seen in the diagram in Slide 42. The biological mechanisms can be counted on to remove about 40 pounds of phosphorus per acre through harvest depending upon the type of crop, frequency of harvest, etc. The chemical mechanisms can be expected to remove and retain almost all of the remaining phosphorus when typical wastewater is applied through an irrigation system. Overland flow and rapid infiltration, while not as effective as irrigation, can be expected to remove more than 60% of the phosphorus if an adequate resting period is provided.